Referee 1:

This manuscript describes a photolytic converter for airborne measurements of NO_2. The focus of the paper is measurements of NO_2 in remote areas where mixing ratios are sub 1 ppb. The authors describe interferences and artefacts associated with a commercial photolytic converter that complicate these sub-1 ppb measurements and suggest modifications to the commercial converter that reduce the effects of artefacts. There is not an overabundance of publications about the nuances of NO_2 photolytic converters, and thus I believe this manuscript can be a value contribution to the atmospheric community.

I agree with the assessments and comments posted by the other referees. I had many of the same concerns. Thus, in an effort to streamline the review process, I have only included my additional thoughts here. I hope they are helpful.

We would like to thank the referee for the feedback and the time to review our manuscript.

Comments:

Title: I do not think that the word "new" is appropriate for the title. This is because there is not anything particularly novel about the modified converter. The use of a fully enclosed quartz cell with and without a reflective Teflon shroud is not new among the airborne research community. However, these PCL systems are typically custom built (e.g., Pollack et al., 2010, Jordan et al., 2020). I wonder if a better title could be "Modification of a commercial photolytic converter for improved aircraft measurements of NO_2 via chemiluminescence".

We thank the referee for this suggestion and have implemented a new title for our manuscript.

Modification of a conventional photolytic converter for improving aircraft measurements of NO2 via chemiluminescence.

Abstract: Please add another sentence or two to the abstract about the aircraft measurement findings related to the NO_2 reservoir species. This is first and foremost in the results section but seems to be lacking mention in the abstract. Also, the abstract is a bit misleading in that it highlights the memory effect as the key phenomenon. Yet, the observations from CAFÉ are likely a combination of phenomena that also include an artefact from the subtraction of two signal channels and a changing background.

We agree with the referee and have added the missing information to the abstract. We would like to highlight that the observed effect which we refer to as memory effect associated with high preceding NO levels and changing humidities induces the observed artifacts and the changing background and summarizes the observed phenomena. More precisely, the instrumental background is increased through high preceding NO levels (almost linear correlation in low concentration NO range (< 0.5 ppb)). Rapid increases in humidity can additionally enhance the release of surface-adsorbed NO molecules and in combination with the low conversion efficiency (introducing a factor of around 5 to the NO2 concentration calculations via Equation (2)) produce the observed artifact signals.

Lines 6 ff.: We find the NO2 reservoir species MPN (methyl peroxy nitrate) to produce the only relevant thermal interference in the converter under the operating conditions

during CAFE Africa. We identify a memory effect within the conventional photolytic converter associated with high NO concentrations and rapidly changing water vapor concentrations, accompanying changes in altitude during aircraft measurements, which is due to the porous structure of the converter material. As a result, NO2 artifacts, which are amplified by low conversion efficiencies, and a varying instrumental background adversely affect the NO2 measurements.

Line 6 and throughout: Maybe it is just me, but I find the use of the word "conventional" to be a bit bothersome. This is because the photolytic converters typically used aboard aircraft do not use the porous Teflon material with ring channel for gas introduction. The word "conventional" seems more appropriate for ground-based applications that utilize commercial monitors and commercial converters. It might help to clarify the difference in the text.

Thank you for pointing this out. We have added some text for clarification and also now refer to the blue light converter as type 1 converter and to the alternative quartz converter as type 2 converter for avoiding confusion.

Lines 132 ff.: We use a blue light converter (type 1) purchased from Droplet Measurement Technologies in 2005 (later Air Quality Design, now Teledyne API) equipped with UV-LEDs emitting at a wavelength of 397 nm (FWHM = 14 nm) which is shown in Figure 1a. The converter was designed for airborne applications.

Line 124: Can you add the year the BLC was purchased from DMT? This could help readers distinguish between the version of "conventional" BLC that you are using compared to other versions of "conventional" commercial BLCs.

The BLC was purchased from DMT in 2005 while its patent was still pending. We have added the year to the text (see above).

Line 134-142: I don't think the use of the words "new" or "newly-developed" are appropriate here since several existing converters already separate the sample flow from direct contact with the porous Teflon surfaces. Maybe a better word for the converter shown in Figure 1b is "modified" or "updated".

We agree with the referee and now refer to the alternative quartz converter as type 2 converter throughout the text.

Section 2.2: I understand the elimination of a night flight (MF11), but why were only MF10 and MF12 through MF15 used in this study? Were MF01 through MF09 not good candidates, was NO_2 data not collected during those flights, or was this phenomenon not observed during those flights?

Unfortunately, NO2 data were not collected for MF01 – MF09 due to instrumental malfunction.

Line 170: Can you add a figure (either here or in the SI) that shows the J-curve for your converters? The conversion efficiencies of the "conventional" BLC (20%) and your "updated" converter (14%) are very low. This is likely a function of your very low cell pressure, which when combined with the high flow rate, results in a short residence time in the photolysis cell. It would be helpful to see how each converter (the conventional versus the updated BLC) behaves over a range of residence times. Regardless, a note

should be included in the text to associate the low conversion efficiency with the low cell pressure, which is needed for high altitude measurements.

We have added text explaining the low conversion efficiency and reasons for the low pressure operation of the photolytic converter. We have added the j-values for the two converters to the text.

Line 143: (j = 0.66 s-1)

Line 150: (j = 0.46 s-1)

Lines 152 ff.: Please note that the low conversion efficiencies in both converters result from the operation at low pressures which we have implemented to pursue aircraft measurements where altitude changes are accompanied by pressure variations. Operating the converter at lower than minimum ambient pressure levels (max. ~ 15km flight altitude) has the benefit of a constant conversion efficiency. On the other hand, a higher conversion efficiency would be desirable for improved accuracy of the measurement.

Line 180: Is it reasonable to utilize a nighttime NO concentration instead of zero measurements for determining c(NO) when the c(NO_2) is determined from the subtraction of the NO measurement from c(NOc) and c($background_{NOc}$) determined from a zero? What is the magnitude of the difference between NO zeros at night versus NO zeros with an overflow of zero air? Has this difference been factored into an uncertainty calculation for c(NO) and c(NO_2)? What is the overall measurement uncertainty for NO and NO_2? Also, what was the concentration and uncertainty of the NO standard used for calibrations. What was the effective calibration mixing ratio after dilution into the sample flow? It would be helpful to add these details to the manuscript.

Thank you for noting the missing information which we have added to the text. We believe that the determination of the instrumental background in the NO channel via nighttime NO measurements is more reliable as there can always be traces of NOx in bottled zero air which additionally vary in concentration between different bottles. For the CAFE Africa field campaign, the instrumental background determined using nighttime measurements was 5 ± 5.3 pptv with a value of 4 ± 7 pptv determined using bottled zero air (for a 1 min integration time), so there was no significant deviation between the two methods. The overall 1σ measurement uncertainty for NO is 6% as described by Tadic et al. (2021). We do not state a measurement uncertainty for NO2 as it was not possible to appropriately evaluate the data due to the described memory effects. The data are not to be used for any scientific conclusions on NO2 concentrations in the upper troposphere and solely serve the demonstration of the problems associated with the conventional blue light converter. The concentration of the secondary NO standard used during the CAFE Africa campaign was 1.187 ± 0.036 ppmv. A flow of 8.6 sccm was diluted in 3.44 SLM of bottled zero air, giving a calibration mixing ratio of 2.97 ± 0.09 ppbv.

Lines 201 ff.: Zero air measurements and NO calibrations using a secondary NO standard (cylinder concentration of 1.187 ± 0.036 ppmv and calibration mixing ratio of 2.97 ± 0.09 ppbv) were performed regularly to determine the variability in the instrumental background and the sensitivity of the channels.

Lines 206 ff.: The NO data were processed as described by Tadic et al. (2021) (5 pptv detection limit at 1 min integration time and 6% relative uncertainty (1σ)). Please note that the instrumental background for the NO data was determined at 5.0 ± 5.3 pptv by a

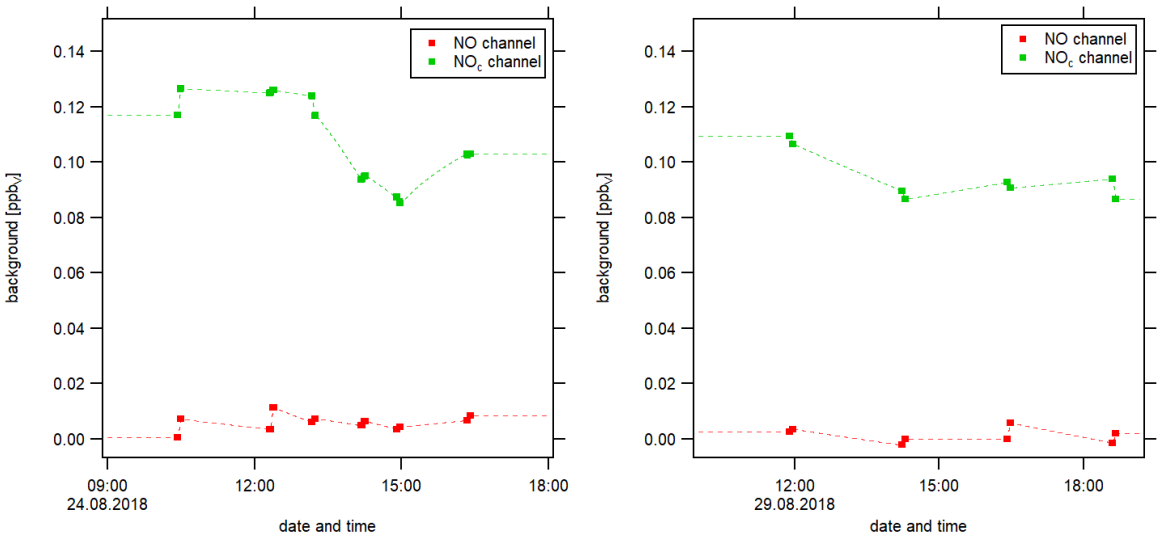
nighttime measurement during measurement flight MF11 on August 26, 2018 of NO as presented by Tadic et al. (2021) and previously described by Lee et al. (2009). The background determined via zero-air measurement was similar with 4 ± 7 pptv (Tadic, 2021).

Line 305: I wonder if the changes in background can be more carefully characterized in a future flight by overblowing the instrument inlet with zero air for the duration of a test flight (aka. a "null" flight). The in-flight instrument performance can be evaluated from changes in the background signal levels during vertical profiles and maneuvers, which can inform about precision, detection limit, motion sensitivity, and fluctuations with pressure and temperature. It can also inform about lags in the recovery of background signals with these perturbations. For high altitude chemiluminescence applications, it might also be interesting to characterize the PMT dark counts versus background in a future test flight by periodically turning off the reagent O3 injection.

Thank you for this interesting thought. Performing a "null" flight could be interesting in regard to determining a stable background signal, which in theory should be constant and independent of ambient conditions. We believe we can achieve this stable background in the NOc channel with the newly implemented quartz converter and hope to pursue this idea in the future.

Line 329: How do the NO_2 measurements change if you assume a constant background signal per altitude level? My first instinct would be that subtracting an interpolated background signal would contribute a good bit to the negative excursions in NO_2. Since the CLD 790 SR has two separate channels, is the BG trace in Figure 5 meant to be the background signal of the NO_2 channel? How does the background of the NO channel differ from that of the NO_2 channel with the LEDs on and off? Does the NO channel background also change with altitude or only the background measured through the converter? Can you add the NO channel BG as a trace in the Figure?

We agree with the referee that in some cases negative NO2 values could result from interpolated background signals. However, we regularly observe negative NO2 values right before and after background measurements during constant flight levels e.g. MF10 between 10:30 and 12:30 or MF12 between 16:30 and 18:00 (BG signal almost constant). Therefore, the background generally being too high due to the described memory effect has a much larger impact on the occurrence of negative values as the interpolation. The background in Figure 5 is the background signal in the NOc channel – we have added this information in the Figure description. The background of the NO channel is usually very close to zero. When switching off the LEDs in the NOc channel, the signal approximates that in the NO channel which we present in Figure S6 of the Supplement. Please note that this experiment was only performed in the laboratory, but should be the same for in-field experiments. The background in the NO channel also showed small changed throughout each flight, but to a significantly smaller extent compared to the variations in the NOc channel:



For a better overview, we decided to show the background in the NO channel in the Supplement and refer to it in the main text.

Lines 361 ff.: In comparison, the background in the NO channel varied between 1 and 11 pptv for MF10 and between -2 and 6 pptv for MF12. We show the instrumental background for MF10 and MF12 in each channel in Figure S3 of the Supplement.

Figure 5: Temporal development of the instrumental background (BG) in the NOc channel, NO, water vapor, and calculated and measured NO2 for measurement flights 10 and 12. (…)

Section 3.1.3: I admit, I found the logic of this section a little hard to follow. If I have this correct, the bulk of the discussion in this section is about the instances when NO2_CLD is enhanced yet there are no enhancements in NO2_PSS nor NO2_DOAS. The authors are claiming that the NO2_CLD enhancements are correlated with increases in water vapor as the aircraft descends. The authors associated the discrepancy to a hysteresis in the photolysis cell upon the introduction of water vapor. If this were the case, then I agree that a decrease in NO_2 back to baseline levels following the increase in water vapor with the lag time representing the memory effect time would be expected. However, the rising edge of the enhancement in NO_2 that starts to increase as a large step change in NO starts to decrease and that occurs earlier in time than the step change in water vapor concentration is not something that I would have expected from a memory effect phenomenon. This leads me to believe that the NO_2 peaks are more of an artefact of the NO channel subtraction, which is enhanced by a factor of 4 due to the correction for Ce, and less so from a memory effect of water vapor on the photolysis cell sampling surfaces.

We respectfully disagree with the referee. The background in the NO channel and the NO measurements of the CLD are accurate and we can therefore be sure that the drop in NO concentration is correct and is also reasonable regarding the vertical atmospheric profile – presented in Figure 2a in Tadic et al. (2021). NO2 concentrations are determined via Equation (4) with the dominating uncertainties on c(NOc) and the instrumental background in the NOc channel. We show in Section 3.2 that the background is at all times too high and the subtraction therefore responsible for the observation of negative NO2 values. Unexpected NO2 peaks must be a consequence of difficulties in the NOc concentration which is most likely related to the memory effect in the photolytic converter. Both effects, negative data through higher than actual

background values and NO2 peaks through humidity induced desorption of (likely) NO, are enhanced by a factor of 4 (=1/Ce), as the referee points out correctly.

From the manuscript (mainly the abstract, introduction, and conclusions), I am led to believe that the authors think the memory effect is the key phenomenon at play with the "conventional" converter. However, the results and discussion of the CAFÉ observations suggest that the signal subtraction, low Ce, fluctuations in background, and large changes in NO concentrations could also have been significant contributors to the observations. Thus, it seems a little misleading to only mention memory effects in the abstract and conclusions. It is my recommendation that the text in the abstract and conclusions be updated to reflect the observations and all possible factors that could have impacted the CAFÉ observations.

As explained above, we consider the term "memory effect" to be the integral of the observed effects. The instrumental background fluctuations in the NOc channel and the problem of always being too high result from storage effects in the blue light converter. Higher preceding NO levels lead to a higher background in the measured concentration range because a short background measurement detects "leaking" NO molecules (and potentially other NOx containing compounds) from the porous converter material. The large NO2 peaks are likely a humidity triggered desorption of NO molecules (or trace gases that are converted to NO) when the aircraft is descending and therefore also related to the memory effects in the converter. The NO measurements in the NO channel yield reliable data and therefore atmospheric variations do not have adverse effects on the calculation of NO2 concentrations. We have added text in the conclusion for clarification.

Lines 513 ff.: More specifically, this includes the subtraction of a fluctuating, higher than actual instrumental background in the NOc channel yielding negative NO2 values as well as humidity triggered spontaneous desorption of stored molecules appearing as large NO2 peaks, both of which effects are amplified by the low conversion efficiency.

Section 3.2: The UV artefact (Figure S5) of 0.1 ppb seems substantial for a sub-1ppb ambient measurement. How does the UV artefact factor into your subtraction calculations (e.g., eq. 4) and into the overall measurement uncertainty? What does Figure S5 look like for the updated converter?

We agree with the referee that the UV artefact for the old converter is highly undesirable. When calculating the NO2 data, we assume that the artefact is equally present for background measurements, calibrations and ambient measurements and is therefore accounted for through the background subtraction. For the alternative quartz converter, the difference between the background with switched on and off LEDs is small and could potentially be due to a trace concentration of NO2 in the zero air gas cylinder which we describe in Lines 158 ff. We have added a Figure to the Supplement to show the effect for the alternative quartz converter and refer to it in the main text.

Lines 487 ff.: For comparison, Figure S6b shows that the effect of switching the LEDs on and off during zero air measurement is marginal when using the type 2 quartz converter.